FEB 19 1968

NASA TECHNICAL MEMORANDUM

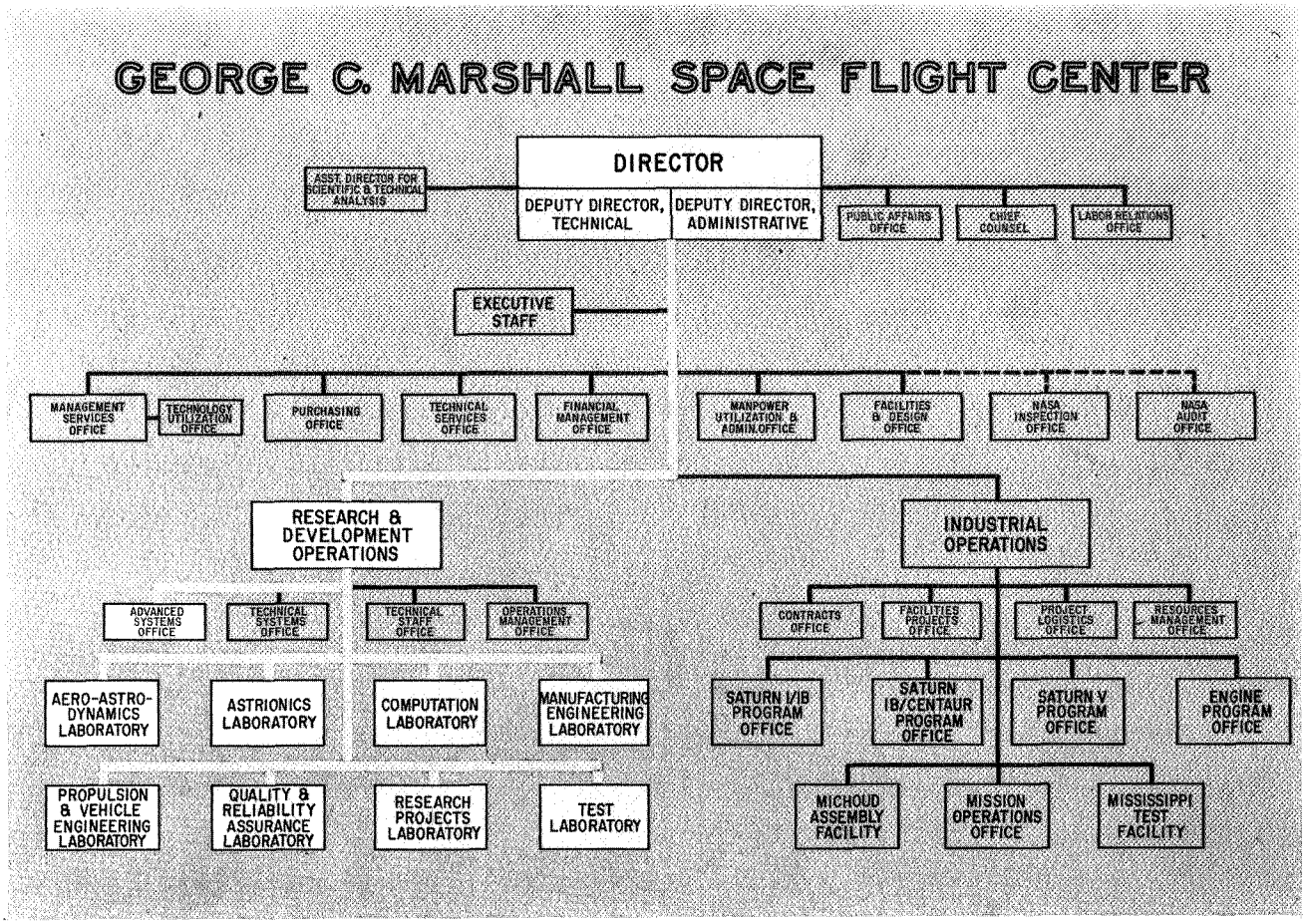
NASA TM X-53383
1965

NASA TM X-53383

PROPERTY OF U. S. AIR FORCE
AEDC LIBRARY
AF 40(600)1200

RESEARCH ACHIEVEMENTS REVIEW SERIES NO. 7

RESEARCH AND DEVELOPMENT OPERATIONS
GEORGE C. MARSHALL SPACE FLIGHT CENTER
HUNTSVILLE, ALABAMA



RESEARCH ACHIEVEMENTS REVIEW SERIES INCLUDES THE FOLLOWING FIELDS OF RESEARCH

1. Radiation Physics
2. Thermophysics
3. Chemical Propulsion
4. Cryogenic Technology
5. Electronics
6. Control Systems
7. Materials
8. Manufacturing
9. Ground Testing
10. Quality Assurance and Checkout
11. Environmental and Aerodynamics
12. Atmospheric Dynamics
13. Instrumentation
14. Power Systems
15. Guidance Concepts
16. Astrodynamics
17. Advanced Tracking Systems
18. Communication Systems
19. Structures
20. Mathematics and Computation
21. Advanced Propulsion
22. Lunar and Meteoroid Physics

NASA TM X-53383

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D. C.

MATERIALS RESEARCH AT MSFC

RESEARCH ACHIEVEMENTS REVIEW SERIES NO. 7

RESEARCH AND DEVELOPMENT OPERATIONS
GEORGE C. MARSHALL SPACE FLIGHT CENTER
HUNTSVILLE, ALABAMA

PROPERTY OF U.S. AIR FORCE
AEDC TECHNICAL LIBRARY
ARNOLD AFB, TN 37389

1965

PREFACE

In 1955, the team which has become the Marshall Space Flight Center (MSFC) began to organize a research program within its various laboratories and offices. The purpose of the program was twofold: first, to support existing development projects by research studies and second, to prepare future development projects by advancing the state of the art of rockets and space flight. Funding for this program came from the Army, Air Force, and Advanced Research Projects Agency. The effort during the first year was modest and involved relatively few tasks. The communication of results was, therefore, comparatively easy.

Today, ten years later, the double purpose of MSFC's research program is still the same. Funding for the program now comes from NASA Program Offices. The present yearly effort represents major amounts of money and hundreds of tasks. The better part of the money goes to industry and universities for research contracts. However, a substantial research effort is conducted in house at the Marshall Center by all of the laboratories. The communication of the results from this impressive research program has become a serious problem by virtue of its very voluminous technical and scientific content.

The Research Projects Laboratory, which is the group responsible for management of the consolidated research program for the Center, initiated a plan to give better visibility to the achievements of research at Marshall in a form that would be more readily usable by specialists, by systems engineers, and by NASA Program Offices for management purposes.

To initiate the plan, monthly Research Achievements Reviews have been established, repetitive over a yearly cycle, with each review covering one or two fields of research. These verbal reviews are documented in the Research Achievements Review Series.

Ernst Stuhlinger
Director, Research Projects Laboratory

This paper presented May 27, 1965

Page intentionally left blank

10-8

TABLE OF CONTENTS

		Page
	SUMMARY	1
I.	INTRODUCTION	1
II.	MATERIALS	2
	A. 1Metals	2
	B. 2Composite Materials	5
	C. 3Lubricants	8
	D. 4Electrical Contact Materials	11
	E. 5Polymers	12
III.	ENVIRONMENTAL EFFECTS AND PROCESSES	16
IV.	CONCLUSIONS	18

LIST OF ILLUSTRATIONS

Figure	Title	Page
1.	Notched/Unnotched Tensile Ratios of Four Wrought-Aluminum Alloys and One Forging	3
2.	Notched/Unnotched Tensile Ratios of Four Wrought-Aluminum Alloys	3
3.	Double-Seal Insulation	6
4.	Ultra High-Strength Composite Materials	7
5.	S-IC Heat Shield	7
6.	Honeycomb Sandwich Construction with M-31 Insulation	8
7.	Resistance of M-31 to Radiant Heating	8
8.	Absolute Spectral Reflectance of M-31	8
9.	Total Normal Emittance of M-31	9
10.	Coefficient of Friction versus Unit Load for MLF-5 and Ease-Off 990	10
11.	Coefficient of Friction versus Temperature for MLF-5 and Fabroid	10
12.	Coefficient of Friction versus Unit Load, Four Lubricants	10
13.	Maximum Allowable Loads for No Welding	11
14.	Photomicrograph of MoS_2-Ag Composite	12
15.	Formation of Silazanes and Silicones	13

Figure	Title	Page
16.	Formation of Cyclic and Linear Silicon-Nitrogen Polymers	13
17.	Condensation Reaction of a Cyclic Silazane	14
18.	Pigmented Silazane as Protective Coating	14
19.	Ordered Silicone-Phenyl Ether Copolymers	14
20.	Diol-Diaminosilane Reaction	15
21.	Weight Loss at High-Temperature Exposure, Hybrid Polymer versus Commercial Adhesive	15
22.	Hybrid Polymer Conversion to High-Temperature Elastomer	15
23.	High-Temperature Exposure, Silphenylene versus Viton A	15
24.	Polybenzoxazole Formation	16
25.	Laminated Cryogenic Seal Development	16
26.	Ultimate Tensile Strength of Teflon	17
27.	Ultimate Tensile Strength of Paraplex P-43	18

LIST OF TABLES

Table	Title	Page
I.	Categories of Materials	1
II.	Saturn V Materials	2
III.	Environmental Effects	2
IV.	Aluminum Alloys	2
V.	Chemical Composition of Experimental Alloys M825 and M826 and Commercial Alloys	4
VI.	Comparison of Mechanical Properties of Experimental Alloys with Commercial Alloys and Goals	4
VII.	Chemical Composition of M-45 and Other High-Strength Aluminum Casting Alloys	4
VIII.	Mechanical Properties of Aluminum Casting Alloys	5
IX.	Magnesium and Magnesium-Lithium Alloys	5
X.	Beryllium and Beryllium-Aluminum Composite	5
XI.	Typical Mechanical Properties of Aluminum Honeycomb	6
XII.	Wire-Reinforced Aluminum Alloy Plates	7
XIII.	Batch Composition of M-31 Thermal Insulation	8
XIV.	MLF-5 Dry-Film Lubricant, MSFC-SPEC-253	9
XV.	Dry-Film Lubricants	9
XVI.	MLF-9 Dry-Film Lubricant	10
XVII.	Wear Rates of Graphite and Graphite/Additive Mixtures	11
XVIII.	Brush Material Compositions	12
XIX.	Wear Rate of Brush Materials	12
XX.	Polymer Applications	13
XXI.	Combined Environmental Testing of Elastomers	17

MATERIALS RESEARCH AT MARSHALL SPACE FLIGHT CENTER

By

W. R. Lucas

SUMMARY

The materials research program at Marshall Space Flight Center (MSFC), which combines in-house and contract work, has resulted in the development and improvement of many materials and techniques, and in the acquisition of new information on the behavior of materials in rocketry and space-flight environments.

The types of materials developed or in a developmental stage encompass a wide range. Some examples are: magnesium-lithium alloys, which are the lightest structural alloys available; wrought- and cast-aluminum alloys with superior strength and toughness at cryogenic temperatures; wire-reinforced, high-strength wrought aluminum; brazed aluminum honeycomb; low-density inorganic insulation for use on large, complexly shaped structures; insulation for cryogens; dry-film lubricants; electrical brush materials for use in vacuum; polymers usable in a new high-temperature range; cryogenic seals and adhesives; and adhesive compatible with liquid oxygen.

The materials research program has been attempting to solve specific problems through these developments. As an additional consequence of this work, it has contributed effectively both to metal and polymer technology and to an understanding of the behavior of materials in entirely new environments.

I. INTRODUCTION

Materials research at MSFC may be called directed research in that it is oriented primarily toward solving current or anticipated problems and toward providing knowledge needed in current or anticipated MSFC programs. Although the investigations which make up the research effort have been divided into in-house and contract tasks, MSFC direction has attempted to coordinate them into a single program. In this way the contracts supplement in-house capability and provide continuity of effort through periods of heavy involvement of MSFC workers in materials engineering. An essential feature responsible for program coordination is the direction of contract tasks by MSFC personnel who are involved directly with similar or related work in MSFC laboratories. Although the discussion of research achievements in this report covers an integral program, any substantial contribution by a contractor is identified by the contract number.

Practically every known type of material is utilized in the broad areas of rocketry and space flight, and many so-called conventional problems become very unconventional in the peculiar environments in which rockets and space vehicles must function. As a consequence, the materials research program has not been limited to structural materials but has been concerned with a very diverse array of applications as shown in Table I. Table II gives a breakdown of materials by quantity used in the Saturn V vehicle. Aluminum is the major structural material. Carbon steel is used primarily for fasteners. Titanium is used for fasteners in the S-IC stage and for pressure bottles in the S-II and S-IVB stages. The stainless steel is used largely for ducts and tubes. The mixed metal category includes components such as valves, black boxes, and instruments containing several materials. The list covers metals, nonmetallic inorganics, and organics. Although metals constitute the largest quantity of materials used, the demands on technology are as great, or greater, for other materials.

TABLE I. CATEGORIES OF MATERIALS

Structural materials
Fasteners and Fittings
Ducts and Tubes
Thermal control materials
Electrical/Magnetic materials
Lubricants
Seals and Gaskets
Adhesives
Encapsulating materials
Working fluids

TABLE II. SATURN V MATERIALS

MATERIAL	MASS PER STAGE, kg (lbm)			
	S-IC	S-II	S-IVB	I. U.
Aluminum	77,587	20,019	5670	567
	(171,047)	(44,133)	(12,501)	(1250)
Carbon steel	2663	55	237	
	(5871)	(121)	(523)	
Stainless steel	1599	2565		9
	(3525)	(5654)		(20)
Titanium	3255	117	61	
	(7176)	(259)	(135)	
Mixed Metals	135	2258	2483	1017
	(298)	(4977)	(5475)	(2243)
Wire/Cables	1699	1472	392	313
	(3745)	(3245)	(864)	(689)
Metal honeycomb	1011			
	(2229)			
Nonmetallic insulation, Fabrics, Fiberglass	742	3937	1045	11
	(1635)	(8679)	(2304)	(25)
Engines	41,922	7736	1554	
	(92,420)	(17,055)	(3427)	
Miscellaneous	510	595	66	
	(1124)	(1312)	(146)	
Paint	191	107	54	5
	(420)	(235)	(120)	(10)
Total	131,314	38,861	11,562	1922
	(289,490)	(85,670)	(25,495)	(4237)

The first selection of materials is usually based on the physical and mechanical properties, but the compatibility of the material with its anticipated environment and the capacity to maintain design properties finally dictate the selection of the material. Thus, later in the discussion research into the environmental effects will be covered, but because of the strong influence of these effects on the development of materials, they are identified here (Table III). These factors distinguish materials science and engineering as applied to rocketry from more conventional applications.

Another factor affecting materials technology is producibility or processibility. Most important developments begin as laboratory curiosities, but these items must be transformed into engineering materials through processing techniques and through a knowledge of the use and application of the material. Some direct routes from the laboratory to the finished product will be demonstrated later in this report.

TABLE III. ENVIRONMENTAL EFFECTS

Temperature Extremes:
Elevated
Sub-Zero (to 20°K, -423° F)
Corrosion
Atmospheric
Galvanic
Stress
Vacuum
Radiation
Meteoroids

II. MATERIALS

The materials investigated in the MSFC research programs are discussed under the categories of metals, composites, lubricants, electrical contact materials, and polymers. Metals, constituting the greatest weight of all materials used, are discussed first. A short review of former applications will help to explain the direction of future work.

A. METALS

The metals discussed here are aluminum alloys, magnesium-lithium alloys, beryllium, and a beryllium-aluminum composite.

1. Aluminum Alloys. Eight aluminum alloys have been used widely in MSFC applications. Some of their properties are shown in Table IV. The utilization of these alloys has paralleled their development in this country, as illustrated in the following review of alloy use. Weldability probably was the most important criterion in the selection of these alloys.

TABLE IV. ALUMINUM ALLOYS

ALLOY	ULTIMATE TENSILE STRENGTH MN/m^2 (ksi)	YIELD STRENGTH MN/m^2 (ksi)	YIELD STRENGTH TO DENSITY RATIO 2540 m (10^5 in.)
5052-H32	214 (31)	145 (21)	2.16
5086-H34	303 (44)	234 (34)	3.54
5456-H343	365 (53)	283 (41)	4.27
2219-T87	427 (62)	345 (50)	4.90
2014-T6	441 (64)	393 (57)	5.64
7075-T6	558 (81)	496 (72)	7.12
7075-T73	483 (70)	421 (61)	6.04
7079-T6	545 (79)	483 (70)	7.07

Alloy 5052 was used in the Redstone missile in section thicknesses up to 3.18 mm (0.125 in.). The newer and better alloy, 5086, which had become available, was used in the Jupiter missile in section thicknesses up to 9.51 mm (0.375 in.). It was planned to use alloy 5456 for a later model of Jupiter (which was not built), but the alloy was used in the first stage of Saturn I in section thicknesses up to 9.51 mm. In the second stage of Saturn I and the second and third stages of Saturn V, alloy 2014-T6 is used. Because the first stage of Saturn V required the welding of section thicknesses of 12.7 mm (0.5 in.) or more, and because fewer welding problems are encountered with alloy 2219 than with alloy 2014 (especially in these thick sections), alloy 2219 was used instead of alloy 2014, although 2219 has a slightly lower strength. The 7000-series alloys have been used primarily in unpressurized areas where fastening can be done mechanically, for example, in the interstage between tanks, and for forgings and fittings. If higher strength alloys become available, they likely will come from the aluminum-magnesium-zinc system. Thus, the need is to develop weldable alloys in this system with acceptable behavior at cryogenic temperatures and with resistance to stress corrosion. Because of the corrosion susceptibility of 7079-T6, its use in heavy forgings has caused difficulty. Alloy 7075-T73, although lower in strength than the other 7000-series alloys listed, is the best from the standpoint of stress corrosion.

Toughness at cryogenic temperature is one of the most important criteria in the selection of the greatest quantity of Saturn structural materials. A satisfactory index as to the fracture toughness of alloys can be achieved by comparing the strength of a notched specimen to that of a smooth specimen. Figure 1 indicates the notched/unnotched ratio of some Saturn alloys. One would desire this ratio to remain as near to 1.0 as possible. Note that the notched/unnotched tensile ratio of 5456-H343 is somewhat inferior to that of the other alloys in this comparison. This is probably due to the comparatively high magnesium content of this alloy. One would not expect to use, at cryogenic temperature, 5000-series aluminum alloys with greater magnesium content than about five percent. This figure shows very clearly that alloy 7079-T6 (as a forging) is not satisfactory for use at the temperature of liquid hydrogen if toughness is required. The notched/unnotched ratios of some 7000-series aluminum alloys are shown in Figure 2. Only alloy 7002 would be suitable for use at liquid-hydrogen temperature if toughness is required.

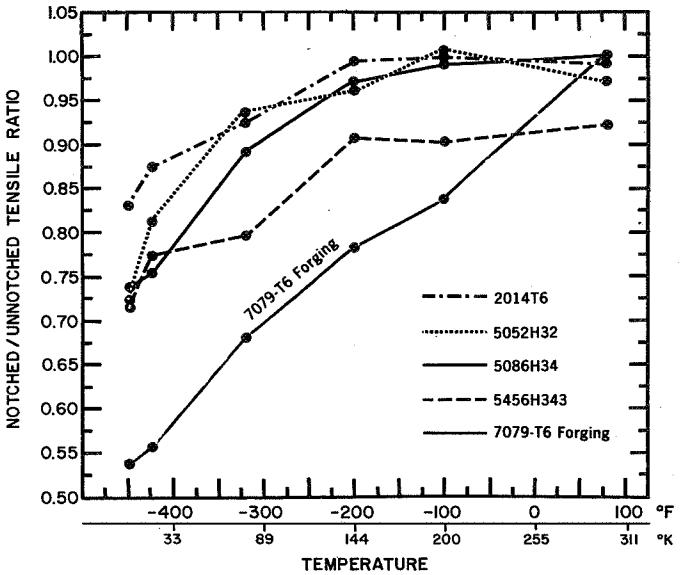


FIGURE 1. NOTCHED/UNNOTCHED TENSILE RATIOS OF FOUR WROUGHT-ALUMINUM ALLOYS AND ONE FORGING

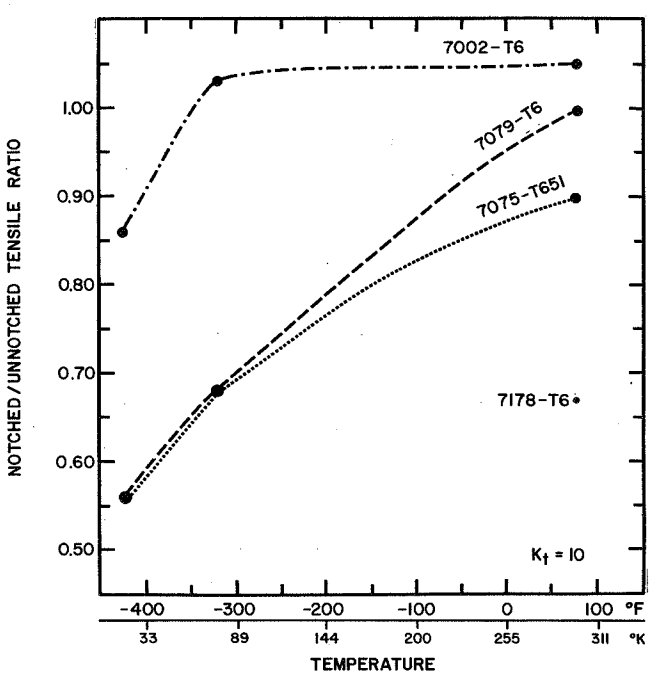


FIGURE 2. NOTCHED/UNNOTCHED TENSILE RATIOS OF FOUR WROUGHT-ALUMINUM ALLOYS

In the belief that useful aluminum alloys of higher strength than is now attainable in weldable alloys can be developed, MSFC is sponsoring a program at Alcoa (NAS8-5452) with the goals of 517 MN/m^2 (75 ksi) ultimate tensile strength, 448 MN/m^2 (65 ksi) tensile

yield strength, 15 percent elongation, and notched/unnotched ratios of 1.0 at room temperature and 0.9 at 20.4°K (-423°F). So far, the aluminum-copper alloy M825 (recently designated X2021) and the aluminum-zinc-magnesium alloy M826 (recently designated X7007) are most promising. In Table V, it is shown that M825 differs from 2219 primarily by the addition of cadmium and tin, and that M826 is a modification of X7106 with respect to content of copper, magnesium, and zinc. In Table VI, the mechanical properties of M825 and M826 are compared with those of commercial alloys and the established goals. It appears that these alloys will meet the strength and toughness criteria. Weldability tests and stress corrosion tests, although encouraging, are inconclusive at this time.

TABLE V. CHEMICAL COMPOSITION OF EXPERIMENTAL ALLOYS M825 AND M826 AND COMMERCIAL ALLOYS

ALLOYING ELEMENT	M825	2219	M826	X7106
Cu	6.3	6.3	0.10	---
Mn	0.30	0.30	0.20	0.20
Mg	---	---	1.8	2.25
Cr	---	---	0.12	0.10
Zn	---	---	6.5	4.25
Ti	0.06	0.06	---	0.03
V	0.10	0.10	---	---
Zr	0.18	0.18	0.12	0.11
Cd	0.15	---	---	---
Sn	0.05	---	---	---
Al	balance	balance	balance	balance

Many aluminum castings are used on the Saturn vehicle, and other castings could be used if better alloys were available. Under contract NAS8-1689 with Battelle Memorial Institute, a heat-treatable aluminum casting alloy (M-45) of high strength and toughness at cryogenic temperatures has been developed. The chemical composition of this alloy is compared with other high-strength aluminum casting alloys in Table VII. Note the difference from alloy 195 with respect to cadmium, silicon, and iron. The mechanical properties of M-45-T6 are compared in Table VIII with those of other aluminum casting alloys in corresponding tempers. This alloy is comparable to alloy 195 in castability. It can be welded to itself and to wrought-aluminum alloys. Recent Saturn castings from this alloy have been found to have ultimate tensile strength of 407 MN/m^2 (59 ksi), yield strength of 359 MN/m^2 (52 ksi), and an elongation of three percent. The material is available from ingot suppliers on special order. Two types of castings, one weighing 42.2 kg (93 lb) and one weighing 0.91 kg (2 lb), are being considered for the S-IVB stage. Several hundred of the latter casting have been made. Rocketdyne is also making experimental castings for possible use on engines.

TABLE VI. COMPARISON OF MECHANICAL PROPERTIES OF EXPERIMENTAL ALLOYS WITH COMMERCIAL ALLOYS AND GOALS

PROPERTY	TESTING TEMP.	M825	M826[1]	2219-T87	X7106-T6351	5456-H343	GOALS
Tensile Strength, MN/m^2 (ksi)	R.T.	519.9 (75.4)	543.1 (79.5)	466.1 (67.6)	452.3 (65.6)	386.8 (56.1)	517.1 (75.0)
	78°K (-320°F)	619.1 (89.8)	636.4 (92.3)	586.1 (85.0)	598.5 (86.8)	497.1 (72.1)	---
	20°K (-423°F)	683.3 (99.1)	---	685.3 (99.4)	706.7 (102.5)	515.7 (74.8)	---
Yield Strength, MN/m^2 (ksi)	R.T.	455.1 (66.0)	497.8 (72.2)	386.1 (56.0)	400.6 (58.1)	306.1 (44.4)	448.2 (65.0)
	78°K (-320°F)	508.8 (73.8)	598.5 (86.8)	466.1 (67.6)	486.1 (70.5)	360.6 (52.3)	---
	20°K (-423°F)	570.9 (82.8)	---	497.8 (72.2)	517.1 (75.0)	377.8 (54.8)	---
Elongation, % in 50.8 mm (2 in.)	R.T.	9.0	12.2	10.5	12.8	10.2	15.0[2]
	78°K (-320°F)	12.7	2.2	11.0	14.0	13.9	---
	20°K (-423°F)	10.0	---	13.5	15.2	7.0	---
Notched/Unnotched[3] Tensile Ratio	R.T.	0.98	1.31	1.13	1.36	0.95	1.0
	78°K (-320°F)	1.06	0.95	1.03	1.06	0.85	---
	20°K (-423°F)	1.03	0.95	0.94	0.94	0.88	0.9

1. 20°K Test Data on M826 Not Complete
2. Recently Changed to 10%
3. $K_t = 10.0$

TABLE VII. CHEMICAL COMPOSITION OF M-45 AND OTHER HIGH-STRENGTH ALUMINUM CASTING ALLOYS

ALLOYING ELEMENT	NOMINAL COMPOSITION[1], MASS PERCENT M-45	A 356	TENS-50	ALMAG 35[2]	195
Cu	3.90-4.50	0.20	0.20	0.01	4.00-5.00
Cd	0.08-0.12	---	---	---	---
Mg	0.06-0.10	0.25-0.40	0.40-0.60	7.00	0.03
Ti	0.02-0.05	0.20	0.10-0.20	0.10	0.20
Si	0.017	6.50-7.50	7.60-8.60	0.10	0.50-1.2
Fe	0.010	0.35	0.40	0.10	0.80
Cr	0.001	---	0.20	---	---
Mn	---	0.10	0.20	0.10	0.20
Zn	---	0.10	0.20	---	0.20
Be	---	---	0.10-0.30	---	---
Al	balance	balance	balance	balance	balance

1. Composition given is maximum permissible unless given as a range
2. Typical

TABLE VIII. MECHANICAL PROPERTIES OF ALUMINUM CASTING ALLOYS

ALLOY	ULTIMATE TENSILE STRENGTH MN/m² (ksi)	TENSILE YIELD STRENGTH MN/m² (ksi)	ELONGATION PERCENT IN 51 mm (2 in.)	CHARPY IMPACT J (ft-lb)
M-45	331(48)	310(45)	5	17.6(13)
A 356	234(34)	200(29)	2	2.7(2)
Tens-50	255(37)	221(32)	2	1.4(1)
Almag 35	207(30)	110(16)	7	4.1(3)
195	207(30)	165(24)	2	4.1(3)

2. Magnesium-Lithium Alloys. The magnesium-lithium alloys are the lightest structural metals commercially available (1.349 g/cm^3, 0.049 lbm/in.^{3}), and applications for these alloys are increasing. Battelle has developed for MSFC two alloys, LA-141 and LAZ-933, which are compared in Table IX. The initial interest in these alloys was their use in the space environment, where corrosion would not be a problem. However, these alloys are now being used for several applications in the earth environment. For example, about 31.8 kg (70 lb) of LA-141 are used in the Saturn V Instrument Unit, and about 2.3 kg (5 lb) are used in an angle-of-attack meter. It is expected that greater use will be made of these lightweight alloys.

TABLE IX. MAGNESIUM AND MAGNESIUM-LITHIUM ALLOYS

	PURE MAGNESIUM	LA 141	LAZ 933
DENSITY, kg/m^3 (lb/in.^{3})	1743.834 (.063)	1356.315 (.049)	1550.075 (.056)
ULTIMATE TENSILE STRENGTH, MN/m² (ksi)	165 (24)	145 (21)	228 (33)
TENSILE YIELD STRENGTH, 0.2% Offset, MN/m² (ksi)	97 (14)	117 (17)	179 (26)
YIELD STRENGTH/DENSITY RATIO, 2540 m (10^5 in.)	2.2	3.5	4.6
MODULUS OF ELASTICITY, 6898 MN/m² (10^6 psi)	6.5	6.5	6.4
MODULUS/DENSITY RATIO, 2540 km (10^8 in.)	1.0	1.3	1.1

3. Beryllium and Beryllium-Aluminum. Beryllium is used in the inertial guidance system of the Saturn V, approximately 75 kg (165 lb) per vehicle. The mass stability required of the gyroscope structures is very high, and only the slightest imbalance is tolerable. The parts must be amenable to polishing to a high surface finish, 0.1 μm (4 μin.) or better and be free from corrosion. Beryllium was chosen for this application because of its dimensional stability, high elastic modulus, high specific heat, high thermal conductivity, low coefficient of thermal expansion, low density, and a high degree of isotropy in the conventional hot-pressed and sintered form. MSFC work has been related to processing of the beryllium powder and to the development of a system for protection against corrosion. Other applications have been considered but none has been implemented yet, primarily because of the brittleness of the material.

A much more potentially useful material for structural applications is the beryllium-aluminum (Be-Al) composite, which is compared with beryllium in Table X. Although the initial development of the Be-Al composite was sponsored by Lockheed, MSFC has contributed to the development (contract NAS8-11448) by the determination of properties of sheet material from production lots. The final report has just been received, and the reproducibility of properties between lots is surprisingly good although only one sheet thickness (1.5 mm or 0.060 in.) was studied. The sheet is now available in dimensions of 0.305 m by 0.61 m (1 ft by 2 ft), but larger sheet sizes will be available.

TABLE X. BERYLLIUM AND BERYLLIUM-ALUMINUM COMPOSITE

	Be SHEET (FROM POWDER)	Be-38%Al SHEET
DENSITY, kg/m^3 (lb/in.^{3})	1826.874 (.066)	2092.601 (.0756)
ULTIMATE TENSILE STRENGTH, MN/m² (ksi)	483 (70)	347 (50.4)
TENSILE YIELD STRENGTH, 0.2% OFFSET MN/m² (ksi)	338 (49)	252 (36.6)
MODULUS OF ELASTICITY, 6898 MN/m² (10^6 psi)	44	29
MODULUS/DENSITY RATIO, 2540 km (10^8 in.)	6.6	3.9

B. COMPOSITE MATERIALS

A class of materials with perhaps more potential than any other is composite materials. Composite materials can be defined so broadly as to encompass practically every engineering material; however, here reference is to the macrostructural level. Sandwich composites will be discussed first. The increasing application of sandwich composites arises from the high strength-to-density ratio and high section modulus or stiffness of most sandwich materials and low thermal conductivity of special sandwich materials. Furthermore, this type of

material allows the maximum flexibility in the utilization of the most favorable properties of each element of the composite.

1. Double-Seal Insulation. The flexibility of sandwich composites can be illustrated by the double-seal insulation concept developed at MSFC to insulate the liquid-hydrogen tank of the S-II stage. This composite consists of a layer of Mylar honeycomb with a Mylar film bonded to one side and aluminum foil bonded to the other, so that each cell of the honeycomb is sealed as shown in Figure 3. To this layer is bonded a perforated phenolic-fiberglass honeycomb core and, finally, aluminum film is bonded to the exterior. The complete composite can be preformed to the appropriate curvature and bonded to the tank wall. The liquid hydrogen evacuates the sealed cells of Mylar honeycomb by cryopumping (condensing and solidifying) and, thus, provides the insulation. The external layer is designed to withstand temperatures up to 492° K (425° F), which are encountered in aerodynamic heating. By being perforated, it can be purged with helium to protect the Mylar core from condensed oxygen, with which it would be incompatible. The thermal gradient across this material may be more than 700° K (800° F). This scheme has been reduced to practice and will be used on flight vehicles.

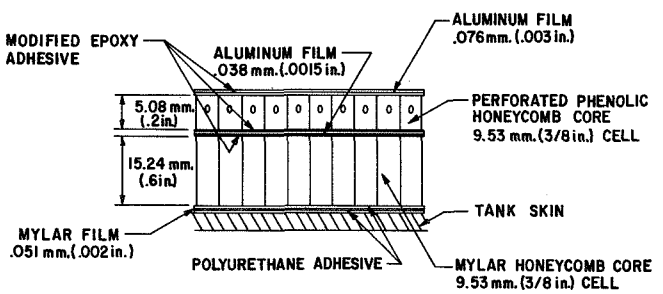

MODIFIED EPOXY ADHESIVE
ALUMINUM FILM .038 mm. (.0015 in.)
ALUMINUM FILM .076 mm. (.003 in.)
5.08 mm. (.2 in.)
15.24 mm. (.6 in.)
PERFORATED PHENOLIC HONEYCOMB CORE 9.53 mm. (3/8 in.) CELL
TANK SKIN
MYLAR FILM .051 mm. (.002 in.)
POLYURETHANE ADHESIVE
MYLAR HONEYCOMB CORE 9.53 mm. (3/8 in.) CELL
MASS = 2.196 kg./m.² (0.45 lbm./ft²)
THERMAL CONDUCTIVITY = 0.0259 joule/m.sec.K° (0.18 Btu in./ft²hr.F°

FIGURE 3. DOUBLE-SEAL INSULATION

The requirements for nondestructive inspection of the dual-seal insulation involved another facet of MSFC work. Based upon this need, MSFC developed an acoustic technique involving both audible and ultrasonic frequency ranges to detect defects of less than one 9.5 mm (0.38 in.) cell diameter. When the acoustical energy echo in two planes is recorded on an x-y type tape, the defect shape can be depicted. The Space and Information Systems Division of North American Aviation is adapting this technique for both the dual-seal cryogenic insulation and the S-II stage common bulkhead in production facilities.

Under contract NAS8-11761, Goodyear Aircraft Company is extending in-house work by modifying the version of the dual seal just described, and is studying related concepts. On another contract, NAS8-11747, Goodyear Aircraft Company is developing materials concepts to be useful as cryogenic insulation and as micrometeoroid bumpers.

2. Nonmetallic Composites. In regard to nonmetallic composites, significant achievements have resulted from contract NAS8-11070. The achievements have been in the development of meaningful physical and mechanical test methods and in the generation of data which are indicative of the true structural potential of fiber-reinforced plastics at cryogenic temperatures.

3. Brazed Aluminum Honeycomb. To avoid the temperature limitations and other deficiencies of adhesive bonding, a task was initiated with Aeronca Manufacturing Corporation (NAS8-5445) to develop a brazed aluminum honeycomb. Considerable success has been achieved. First, it has been demonstrated that aluminum face sheets can be brazed to aluminum core. Second, it has been shown that the composite can be strengthened by quenching directly from the brazing furnace into liquid nitrogen with a minimum of distortion. Typical room-temperature mechanical properties of brazed and adhesively bonded aluminum face sheet (X7106) and core (6951) are shown in Table XI. The increase in core shear strength is due to the fact that this aluminum core normally is not heat treated. The strength differentials would be more favorable at elevated temperatures and at cryogenic temperatures. Work is continuing with other high-strength aluminum alloys and in improving processes.

TABLE XI. TYPICAL MECHANICAL PROPERTIES OF ALUMINUM HONEYCOMB*

	FLATWISE TENSILE kN/m² (psi)	FLATWISE COMPRESSION kN/m² (psi)	EDGEWISE COMPRESSION kN/m² (psi)	CORE SHEAR kN/m² (psi)
BRAZED	13,100 (1900)	8270 (1200)	468,840 (68,000)	8960 (1300)
ADHESIVE BONDED (FM 1000)	5515 (800)	8270 (1200)	379,210 (55,000)	4830 (700)

* Face Sheets: X7106: 1.57 mm (0.062 in.) thick
Core: 6951: 15.24 mm (0.6 in.) thick

4. Wire-Reinforced Aluminum. Another type of composite material being investigated is metal-fiber- or wire-reinforced wrought aluminum and aluminum castings. Significant progress in the

work has been made recently through contract NAS8-11508 with Harvey Aluminum Company. The purpose of this investigation is to produce wire-reinforced aluminum in thicknesses of 6.35 mm (0.25 in.) and 19 mm (0.75 in.) having a minimum tensile strength of 1.2 GN/m^2 (175 ksi) and a maximum density of 3.986 g/cm^3 (0.144 lbm/in.^{3}). This density results from a volume percentage of 75 percent aluminum and 25 percent steel. Small samples up to 19 mm thick have been produced with fairly uniform distribution of the reinforcement wire in the aluminum matrix, as shown in Figure 4. These plates were made by pressing the reinforcing wire into thin sheets and then laminating the sheets. Although the wires in these samples are unidirectional, it is not necessary that they be this way using the current

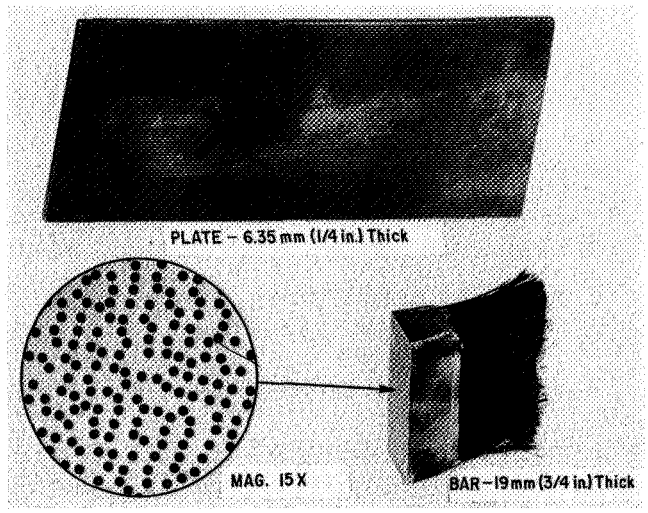


FIGURE 4. ULTRA HIGH-STRENGTH COMPOSITE MATERIALS

technique. The aluminum alloys which have been used and corresponding tensile strengths obtained from the composite are shown in Table XII. In each case, the reinforcing wire is AM-355 with an approximate diameter of 0.254 mm (0.010 in.) and an approximate tensile strength of 3.45 GN/m^2 (500 ksi). The contractor is prepared now to produce plates 0.3 m (12 in.) wide by 2.4 m (96 in.) long, and is expected to deliver some of these plates in July 1965. Study is continuing on development of the material and on joining techniques. Plates have been joined by diffusion bonding with an efficiency of 92 percent.

5. M-31. Another type of composite material was developed specifically for the heat shield of the S-IC stage of Saturn V. This material, known as M-31, was developed to be low in density, to have

TABLE XII. WIRE-REINFORCED ALUMINUM ALLOY PLATES

ALUMINUM MATRIX	COMPOSITE CONDITION	ULTIMATE TENSILE STRENGTH, MN/m^2 (ksi)
5456	as fabricated	945 (137)
2024	sol. ht. treated, cw 3% aged, cw 3%	1193 (173)
2219	sol. ht. treated, cw 3%, aged	1093 (158.5)
7075	sol. ht. treated, cw 3%, aged	1200 (174)
7178	sol. ht. treated, cw 2% aged, cw 2%	1210 (175.5)

low thermal conductivity, to be nonburning, and to be applied easily by trowel and cured at relatively low temperatures. The composition of the material as developed is shown in Table XIII. Tipersul is a trade name of E. I. du Pont de Nemours and Company and consists of fibrous potassium titanate. Ludox is colloidal silica. Figure 5 is a diagram of a section of honeycomb heat shield to which M-31 is applied.

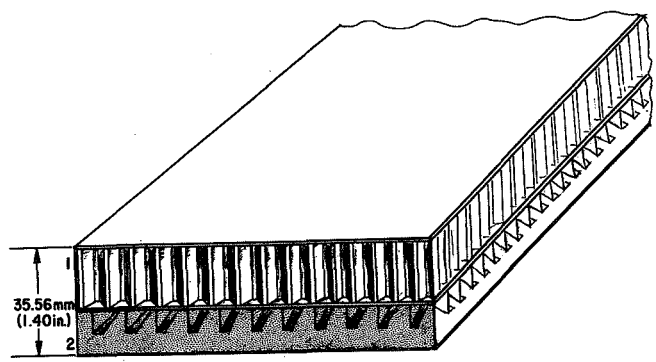

35.56mm (1.40in.)
1
2
1. 25.4mm (1.000 in.) 15-7 PH BRAZED S.S. 4.76 mm (3/16 in.) HONEYCOMB
2. 10.2mm (0.400in.) 15-7 PH BRAZED 3.68 mm (0.145 in.) EDGE ROLLED

FIGURE 5. S-IC HEAT SHIELD

The metallic part of the heat shield consists of a stainless-steel honeycomb which serves as the load-carrying member, and a crimped, open-face honeycomb brazed to the load-carrying member. M-31 is applied to the open face as plaster is applied to a wall (Fig. 6). The completed assembly is dried at approximately 344°K (160° F). As applied to the S-IC stage of Saturn, the mass of the composite is about 10.3 kg/m^2 (2.1 lbm/ft^2). The density of M-31 can be varied between 753 kg/m^3 (47 lbm/ft^3) and 881 kg/m^3 (55 lbm/ft^3).

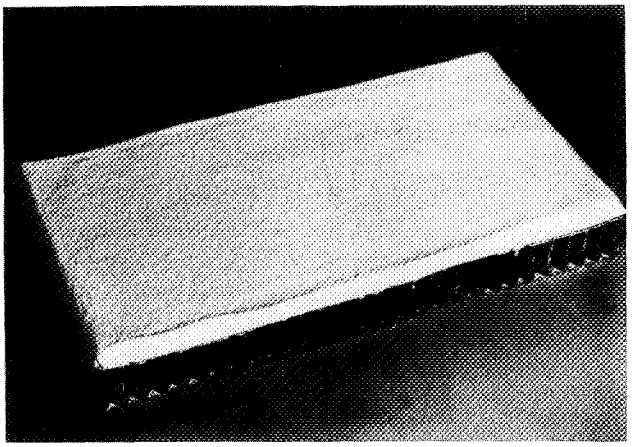


FIGURE 6. HONEYCOMB SANDWICH CONSTRUCTION WITH M-31 INSULATION

TABLE XIII. BATCH COMPOSITION OF M-31 THERMAL INSULATION

MATERIAL	PARTS BY WEIGHT
"Tipersul" block	90
Asbestos fibers	10
"Ludox" HS	420

The effectiveness of M-31 in a radiant environment is shown in Figure 7, in which the temperature rise at the back surface of a sheet-steel blank 1 mm (0.040 in.) thick is compared to that at the back surface of a coating of M-31 8.1 mm (0.320 in.) thick when both were exposed to a heat flux of 272 kW/m^2 (24 Btu/ft^2 sec). M-31 has been shown to be an effective insulator in radiant heating environments up to 794 kW/m^2 (70 Btu/ft^2 sec). The material is also an effective insulator in a convective environment. Optical properties of interest are essentially constant; absolute spectral reflectance is illustrated in Figure 8, and total normal emittance in Figure 9.

Illinois Institute of Technology Research Institute has a contract (NAS8-11333) to develop improved lightweight insulation materials for tail heating protection, and significant progress has been reported on ceramic foams which are being thermally and structurally optimized now.

C. LUBRICANTS

The problem of lubrication in the vacuum of space has been one of the most pressing ones, particularly for intermittently moving parts. Mating metal parts tend to weld together in the space environment. This appears to be particularly true when

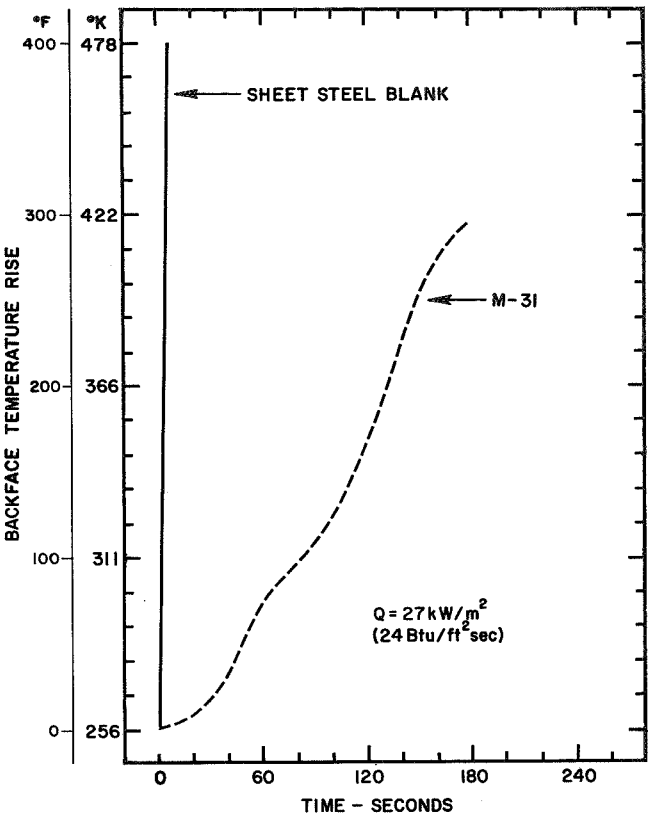


FIGURE 7. RESISTANCE OF M-31 TO RADIANT HEATING

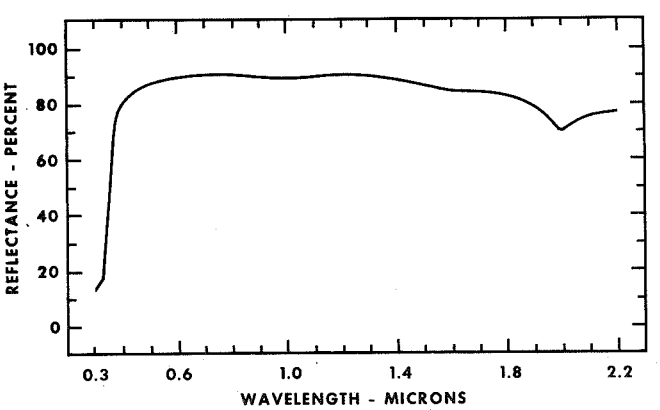


FIGURE 8. ABSOLUTE SPECTRAL REFLECTANCE OF M-31

mating parts are of the same material or when of different materials and one of the materials tends to form a stable, solid solution in the other. Exposure of clean surfaces either by plastic deformation or by some other means such as ion bombardment can result in extreme friction and seizing of mating surfaces even at modest vacuum. Moreover, the better known organic lubricants will be subject to evaporation in space, or they may be degraded by irradiation.

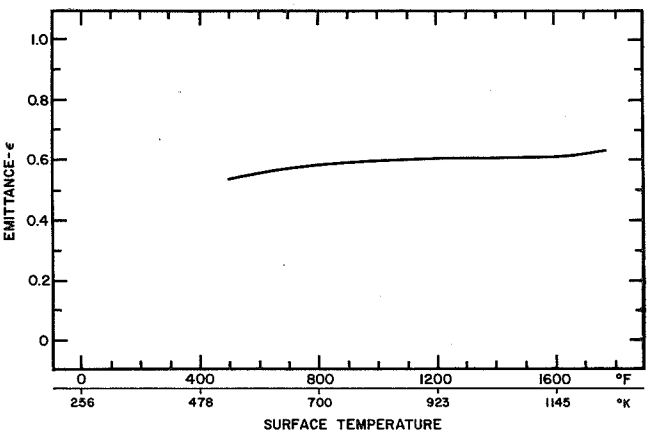


FIGURE 9. TOTAL NORMAL EMITTANCE OF M-31

1. Dry-Film Lubricants. The first significant contribution by MSFC to the dry-film lubricant field was the lubricant, MLF-5. MLF-5 was developed to MSFC requirements by Midwest Research Institute under contract NAS8-1540 and was evaluated by MSFC (described in MSFC-SPEC-253). Some of its features are listed in Table XIV. This lubricant now is being used on the RL-10A3 engine gimbal bearing on the S-IV stage of Saturn I and the Centaur because the lubricants used initially were shown to be unsatisfactory for vacuum operations. A comparison of MLF-5 with some better dry-film lubricants is given in Table XV. All except graphite were tested under uniform conditions. Although the graphite was tested under a higher load (75.8 kN/m^2 or 11 psi compared to 15.2 kN/m^2 or 2.2 psi for the others) and a higher speed (8.1 m/sec or 1600 fpm compared to 3.9 m/sec or 765 fpm for the others), the results substantiate the generally accepted conclusion that graphite is an ineffective lubricant in vacuum because of the absence of oxygen and moisture on the surfaces of the graphite flake.

TABLE XIV. MLF-5 DRY-FILM LUBRICANT, MSFC-SPEC-253

PREPARATION:

	INGREDIENT	PARTS
1.	Molybdenum disulfide	10
2.	Graphite	1
3.	Gold	5
4.	Sodium silicate	7
5.	Water	60

APPLICATION:

Spray and bake

ADVANTAGES:

1. Extreme pressure
2. Constant, low friction
3. Not sensitive to environment
4. LOX compatible
5. Moisture resistant

TABLE XV. DRY-FILM LUBRICANTS

LUBRICANT	BINDER	COEFFICIENT OF FRICTION (AVERAGE) 101 kN/m^2 (760 torr)	COEFFICIENT OF FRICTION (AVERAGE) 133 μN/m^2 (1×10^{-6} torr)
Gold	Electroplated	0.21	0.24
MoS_2	Teflon	0.25	0.25
MoS_2	Na_2OSiO_2	0.21	0.35
MoS_2/Graphite (10:1)	Na_2OSiO_2	0.21	0.26
MLF-5	Na_2OSiO_2	0.17	0.10
Graphite[1]	---	0.15	0.70[2]

1. From Ramadanoff & Glass
2. 1333 N/m^2 (10 torr)

In Figure 10, the coefficient of friction of MLF-5 as a function of bearing pressure in vacuum is compared with that of Ease-Off 990, the commercial lubricant originally specified for the RL-10A3 gimbal bearing. In Figure 11, the coefficient of friction of MLF-5 as a function of temperature in vacuum is compared with that of Fabroid, the commercial lubricant currently specified for the J-2 engine gimbal bearing. Inasmuch as Fabroid is a glass-reinforced Teflon, higher bearing pressure would be expected to show Fabroid less favorably.

The utility of dry-film lubricants is not restricted to space-related applications. The Saturn V hold-down arms will be lubricated with a new related compound, MLF-9, described in Table XVI. The choice of this lubricant for the hold-down arms was based on data such as shown in Figure 12. Experi-

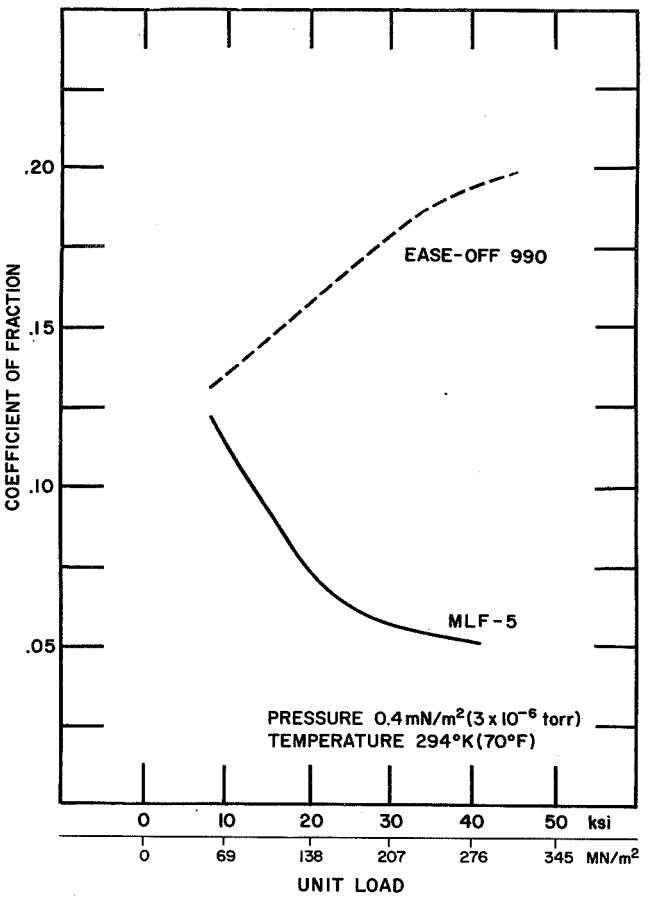


FIGURE 10. COEFFICIENT OF FRICTION VERSUS UNIT LOAD FOR MLF-5 AND EASE-OFF 990

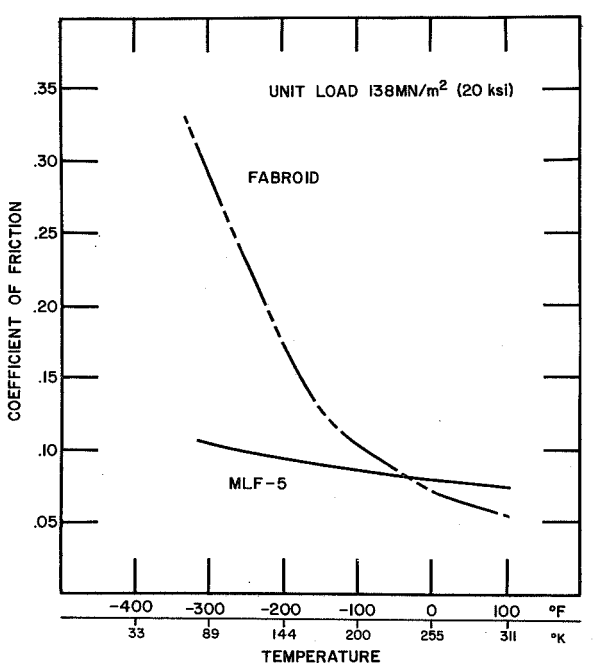


FIGURE 11. COEFFICIENT OF FRICTION VERSUS TEMPERATURE FOR MLF-5 AND FABROID

TABLE XVI. MLF-9 DRY-FILM LUBRICANT

PREPARATION:

INGREDIENT		PARTS
1.	Molybdenum disulfide	10
2.	Graphite	1
3.	Bismuth	14
4.	Aluminum phosphate	9
5.	Water	60

APPLICATION:

Spray and bake

ADVANTAGES:

1. Extreme pressure
2. Constant, low friction
3. Not sensitive to environment
4. LOX compatible
5. Moisture resistant

mental data on commercial greases and the special lubricants, MLF-5 and MLF-9, some of which are plotted here as coefficient of friction versus bearing pressure, demonstrated clearly the superiority of dry films over greases at the bearing pressures of concern (more than 689 MN/m² or 100 ksi) in the

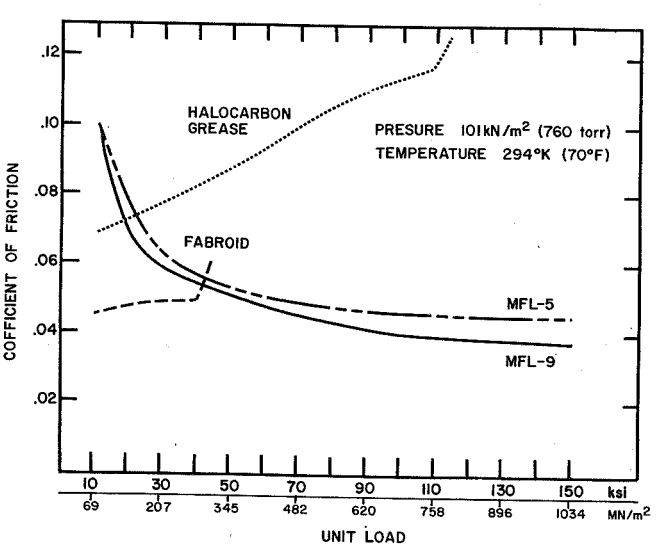


FIGURE 12. COEFFICIENT OF FRICTION VERSUS UNIT LOAD, FOUR LUBRICANTS

Saturn V hold-down arm application. In addition to having a somewhat more favorable coefficient of friction than MLF-5, MLF-9 is not hygroscopic as is MLF-5. The substitution of bismuth for gold also reduces the price of MLF-9.

2. Cold-Welding Problem. An interesting adjunct to the lubrication studies has been the work on the "cold welding" of metals in vacuum. Much concern has been expressed over the possible welding of metals, cleaned by long exposure to space, when they come into contact, such as in a docking operation. Under contract NAS8-11066, Hughes Aircraft Company developed the data shown in Figure 13. This chart depicts loads which can be tolerated without causing "welding" of representative materials when exposed to a pressure of 667 nN/m^2 (5×10^{-9} torr) for 19 hours. The samples were cleaned chemically before they were loaded in vacuum. Results of this program demonstrate that in essentially all cases no "cold welding" occurred at static loads of up to 75 percent of the compressive yield strength of the materials. However, under dynamic loads, the mechanical cleaning caused by vibration may enhance the "cold welding" prospects, but the existence of any non-metallic inorganic film (e.g., a surface oxide) on either faying surface will preclude the possibility of "welding." These data indicate that the problems of "cold welding" during docking maneuvers may not be severe.

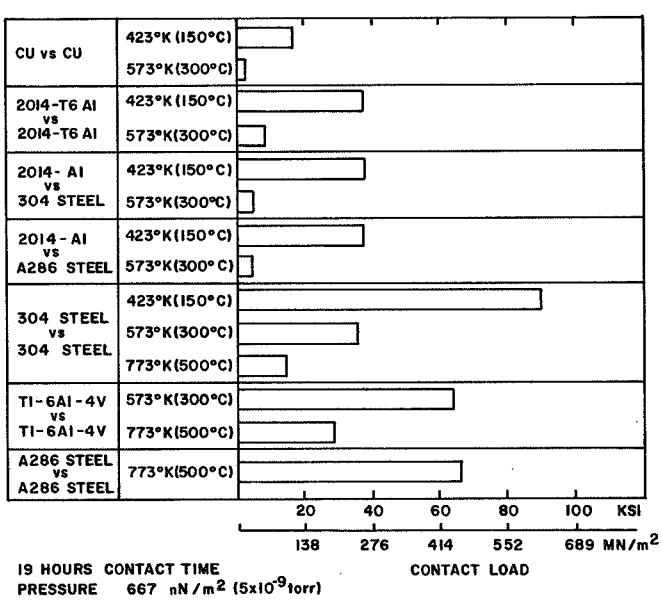


FIGURE 13. MAXIMUM ALLOWABLE LOADS FOR NO WELDING

D. ELECTRICAL CONTACT MATERIALS

The deficiencies of commercial sliding contact material (slip rings and brushes) in the space environment have been thoroughly established. The complexities involved in circumventing these problems by using ac power, and the sacrifices realized by neglecting the attributes of dc equipment, prompted MSFC to embark on a program to develop sliding contact materials applicable to the space environment.

In a vacuum environment, the problem with standard graphite brushes is excessive wear rate, as illustrated in Table XVII. The additives developed for airplane flight altitudes are not adequate for space flight. It was shown in the vacuum lubrication program that molybdenum disulfide is a good lubricant in vacuum; however, it is not an electrical conductor. To utilize the lubricity in vacuum of molybdenum disulfide, a composite of MoS_2 and metallic powder was prepared.

TABLE XVII. WEAR RATES OF GRAPHITE AND GRAPHITE/ADDITIVE MIXTURES

MATERIAL	PRESSURE N/m^2 (torr)	DURATION hours	WEAR RATE mm/hr (in./hr)
Graphite	101 k (sea level)	---	0.0025
	(760)		(1×10^{-4})
Graphite	30 k (9 km)	6	2.54
	(225) (30,000 ft)		(1×10^{-1})
Graphite plus Halide additive	30 k (9 km)	112	101.6
	(225) (30,000 ft)		(4×10^{-3})
Graphite plus MoS_2 pockets	30 k (9 km)	---	7.6
	(225) (30,000 ft)		(3×10^{-4})
Graphite	133 μ (152 km)	0.5	30.48
	(1×10^{-6}) (500,000 ft)		(1.2)
Graphite plus Halide additives	133 μ (152 km)	1.5	8.89
	(1×10^{-6}) (500,000 ft)		(3.5×10^{-1})
Graphite plus MoS_2 pockets	133 μ (152 km)	16	0.51
	(1×10^{-6}) (500,000 ft)		(2×10^{-2})

Both silver and copper were evaluated as the metal powder. The processing technique involved hot-pressing the mixed powder to a dense, composite material capable of being ground to any desired geometric shape. To date, the most successful compositions have been prepared at a temperature of 1200°K (1700° F) and a pressure of 27.6 MN/m^2 (4000 psi). Compositions containing volume percentages shown in Table XVIII have been evaluated, and results indicate that a composition of 14 percent Ag-86 percent MoS_2 represents the most desirable lubrication and conductivity compromise. The conduction of these

TABLE XVIII. BRUSH MATERIAL COMPOSITIONS

COMPOSITION NUMBER	VOLUME PERCENT				
	MOLYBDENUM DISULFIDE	SILVER	COPPER	TUNGSTEN DISULFIDE	SILVER SULFIDE
1	95		5		
2	90		10		
3	80		20		
4	90	10			
5	86	14			
6	80	20			
7	73.5	26.5			
8	61.8	38.2			
9	82.5	14.5	3		
10	74.2	20			5.8
11	60	30			10
12		18		82	
13		23.7		76.3	
14				67	33

composites has been studied, and indications are that the composite does not contain sufficient metal atoms to permit metallic conduction. Although this is not conclusive evidence, the photomicrograph of the composite (Fig. 14) indicates that the silver particles are not connected. Furthermore, the electrical conductivity is less than that of silver. A semiconducting

FIGURE 14. PHOTOMICROGRAPH OF MoS_2-Ag COMPOSITE

process may be involved in the composite brush to provide electrical conductivity between the silver particles. Work is being done now to verify this possibility. There is experimental evidence that the 14 percent Ag-86 percent MoS_2 composite brush will function satisfactorily in pressures as low as 133 nN/m^2 (10^{-9} torr). Brushes have been run in excess of 7000 hours continuously without failure in simulated commutator tests and have been run in 75-watt (1/10 hp) motors successfully for a total of 5580 hours. Preliminary testing has been completed successfully on 186-watt (1/4 hp) motors. A comparison of the wear rate of these brushes with other experimental brush materials and with commercial brushes is shown in Table XIX. The composite-brush wear rates at 304,800 meters (1 million feet) are less than the wear rates (2.54 μm) of commercial brushes at 0.1 MN/m^2 (1 atm), as shown in Table XVII. There is no reason to believe that these composite brushes would not be applicable to motors of much higher power than have been tested. As indicated by MSFC's experimental program, the dc motor can be used efficiently in space or on the surface of our moon or other planets.

TABLE XIX. WEAR RATE OF BRUSH MATERIALS

MATERIAL	PRESSURE $\mu N/m^2$ (torr)	DURATION hours	WEAR RATE mm/hr (in./hr)
Graphite	133 at 152 km	0.5	30.48
	(1×10^{-6} at 500,000 ft)		(1.2)
Graphite plus Halides	133 at 152 km	1.5	8.89
	(1×10^{-6} at 500,000 ft)		(.35)
Graphite plus MoS_2 pockets	133 at 152 km	16	0.508
	(1×10^{-6} at 500,000 ft)		(.02)
MoS_2 - Ag Hot pressed material	13.3 at 305 km	6,914	0.03556 μ
	(1×10^{-7} at 1 million ft)		(1.4×10^{-6})

E. POLYMERS

Many materials of critical interest to MSFC fall in the category of polymers; structural adhesives, plastics, and synthetic rubber are common examples. Some applications of polymers to MSFC work are listed in Table XX.

A polymer may be described as an assemblage of long, chain-like molecules. These molecules are built up of repetitive identical linkages or chemical building blocks which are induced to couple together during a chemical reaction. Actually, one obtains a statistical distribution of chain lengths or molecular weights which depends upon the nature of the materials and the process used to prepare the polymer. It is possible in most cases to ascertain experimentally an average molecular weight.

TABLE XX. POLYMER APPLICATIONS

ADHESIVES
1. Bonding clips, Brackets
2. Bonding composite materials
SEALING AND ENCAPSULATING
1. Seals, Gaskets, Valve seats
2. Conformal coatings, Potting
COMPOSITES (STRUCTURAL AND INSULATION)
1. Reinforced plastics (laminates, filament wound)
2. Foams
3. Films
4. Honeycomb cores
COATINGS
1. Temperature control
2. Corrosion protection
LINERS AND BLADDERS
1. Propellant expulsion
2. Fluid containment

At the molecular level, a linear polymer may be compared with a bucket of worms. The long, worm-like molecules would be coiling and tangling around one another in continuous motion; the extent and frequency of this motion would be dictated by the temperature and other factors. It is this capacity for relatively free molecular motion, as compared with metals and ceramics, which confers unique physical properties on the polymer solid state. These properties can be regulated in many instances by what we call the degree of crosslinking or the number of times an average worm-like molecule is attached to one of its neighboring molecules. If there are no attachment points along any of these continuous molecular chains, the material may be a linear polymer like Teflon, which readily undergoes permanent plastic deformation. With only a moderate degree of crosslinking, the molecular lattice develops an elastic memory and tends to return to its original form when a stress is removed. This material may be an elastomer or rubber and, in this case, the crosslink density is usually slightly over unity. If this crosslinking can be continued further, a highly complex three-dimensional molecular array can be developed that will be characterized by extreme strength and rigidity. An attempt is made to achieve this highly crosslinked state in structural adhesives during the curing step. In fact, curing can be defined as a chemically controllable process for increasing the crosslink density.

1. Polymers for High-Temperature Application. A combined program of internal and contractual work was started several years ago for the study of polymers containing silicon-nitrogen bonds. This type of polymer is compared with silicones in Figure 15. As shown, starting with silicon dihalides, a silicone results through reaction with water, or a silazane (silicon-nitrogen polymer) through reaction with ammonia. The high-temperature properties of silicones are well known, and it was expected, and now appears, that silazanes will have substantially better high-temperature properties. Furthermore, silazanes serve as intermediates, as will be demonstrated later, to make polymers of still higher-temperature utility.

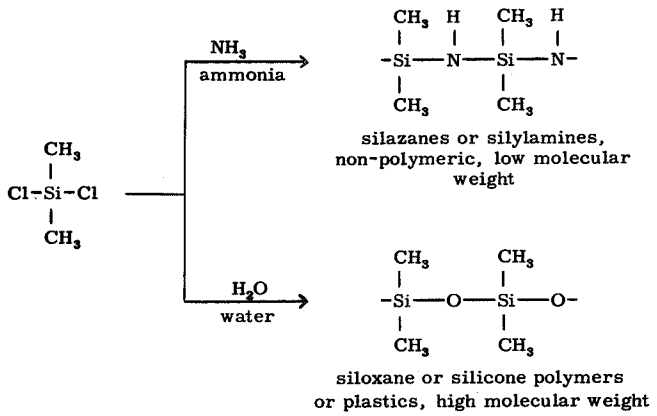


FIGURE 15. FORMATION OF SILAZANES AND SILICONES

The current joint effort in this area with Southern Research Institute has elicited a great deal of interest. Both linear polymers and cyclic compounds have been prepared by direct reactions such as those shown in Figure 16. A direct halosilane-amine reaction can be used to produce cyclic compounds or low molecular-weight silazane polymers. In addition, these materials can be modified by reactions involving an exchange process between a Si-N compound or polymer and an organic diamine.

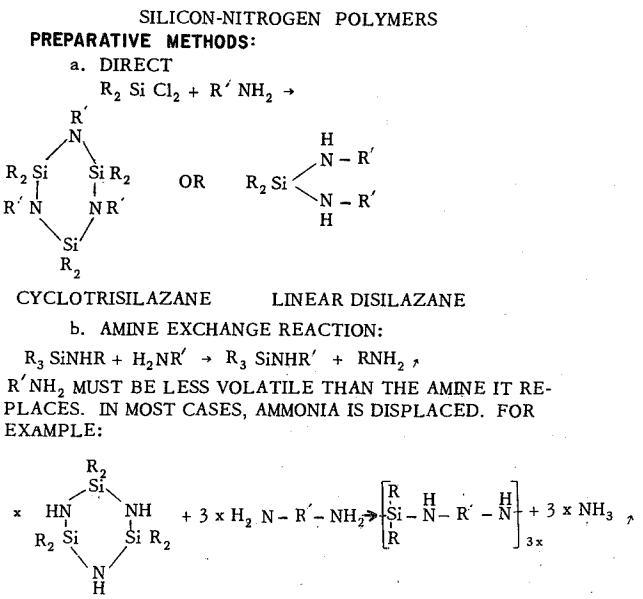

SILICON-NITROGEN POLYMERS
PREPARATIVE METHODS:
a. DIRECT
R2 Si Cl2 + R′ NH2 →
OR
CYCLOTRISILAZANE
LINEAR DISILAZANE
b. AMINE EXCHANGE REACTION:
R3 SiNHR + H2NR′ → R3 SiNHR′ + RNH2 ,
R′NH2 MUST BE LESS VOLATILE THAN THE AMINE IT REPLACES. IN MOST CASES, AMMONIA IS DISPLACED. FOR EXAMPLE:
+ 3 x H2 N – R′ – NH2
+ 3 x NH3 ,

FIGURE 16. FORMATION OF CYCLIC AND LINEAR SILICON-NITROGEN POLYMERS

Some of the cyclic silazanes have the property of undergoing complex condensation reactions at elevated temperatures (Fig. 17). The brown, benzene-soluble resin is tractable up to 793° K (520° C), but, at this temperature, it suddenly undergoes a condensation reaction, producing a porous, intractable polymer which is stable to about 973° K (700° C). Although the ultimate products of these reactions are extremely stable materials, there are drawbacks to their immediate use that will necessitate further development. One potential application for this type

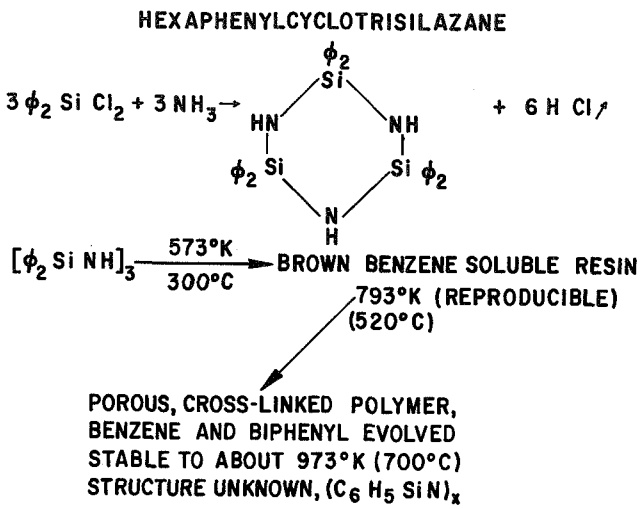


FIGURE 17. CONDENSATION REACTION OF A CYCLIC SILAZANE

of polymer is in protective coatings. Some work has been done to test this potentiality. Aluminum panels were coated with pigmented (Al and TiO_2) silazane coatings and held at 673° K (400° C) for four hours. Only the middle portions of the panels were coated, and the edges were exposed. At the temperature of exposure, the aluminum is so soft that it must be supported. Following the temperature exposure, the panels were exposed 14 days to a standard salt-spray test for protective coatings. As shown in Figure 18, the coated areas were not affected appreciably by this treatment.

A development that originated at MSFC was the evaluation of simple silazane compounds as intermediates for the formation of other polymers. Figure 19 indicates how silazanes can be used to prepare an extremely interesting family of hybrid polymers. These are half ether and half silicone, and the ordered spacing of these units down the chain length offers interesting possibilities for the development of crystalline order. The structural formula of a specific polymer of this family is given in Figure 20, and an outstanding property of this material is shown in

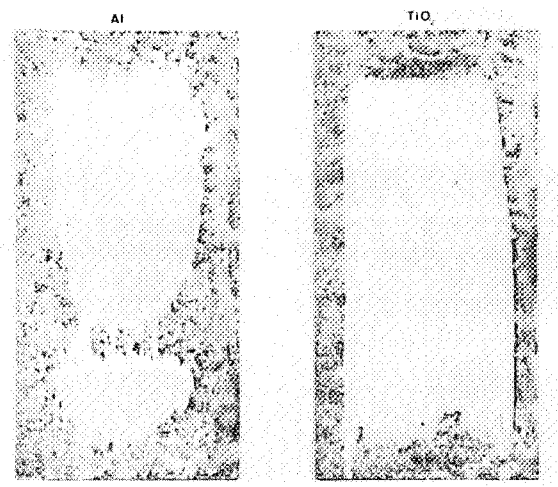
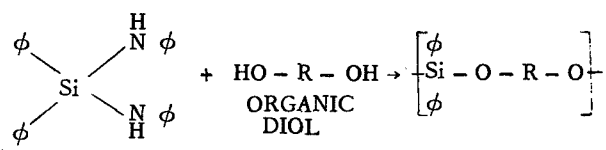


FIGURE 18. PIGMENTED SILAZANE AS PROTECTIVE COATING

INTERNAL RESEARCH

ORDERED SILICONE-PHENYL ETHER COPOLYMERS



DISILAZANE

PROPERTIES:

GOOD THERMAL STABILITY
GOOD FILM FORMING PROPERTIES
SOLUBILITY
RESISTANT TO ULTRAVIOLET RADIATION (?)

FIGURE 19. ORDERED SILICONE-PHENYL ETHER COPOLYMERS

Figure 21. This shows the weight loss of the hybrid polymer under a uniformly programed rate of temperature rise in comparison with a commercial polybenzimidazole adhesive which may represent the ultimate thermal stability obtainable in a practical adhesive system. The polymer prepared locally is relatively stable and, on the basis of this behavior, it is being studied intensively to further define its high-temperature potential. The polymer has been made into fiber and film, and is being studied now as an "organic solder" in the hope that it can be converted into a crosslinkable adhesive. Full details of this work were reported by Curry and Byrd of the Materials Division (Propulsion and Vehicle Engineering Laboratory, MSFC) in Journal of Applied Polymer

Science (vol. 9, 1965), and this publication has aroused considerable interest in the future of these materials.

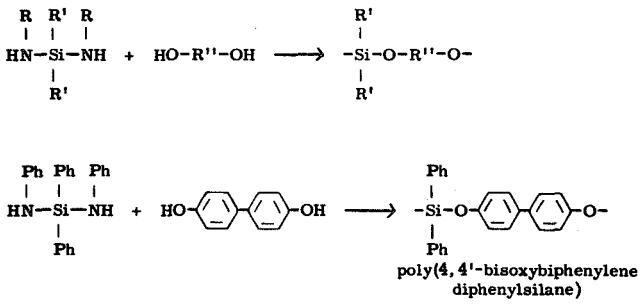


FIGURE 20. DIOL-DIAMINOSILANE REACTION

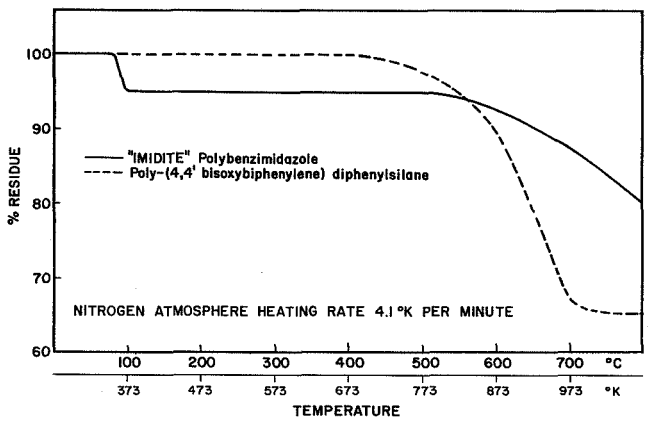


FIGURE 21. WEIGHT LOSS AT HIGH-TEMPERATURE EXPOSURE, HYBRID POLYMER VERSUS COMMERCIAL ADHESIVE

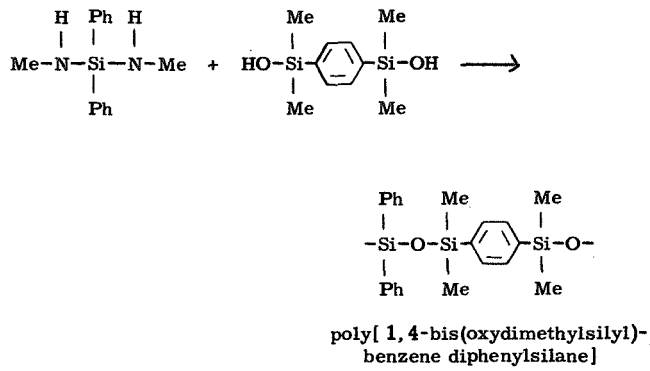


FIGURE 22. HYBRID POLYMER CONVERSION TO HIGH-TEMPERATURE ELASTOMER

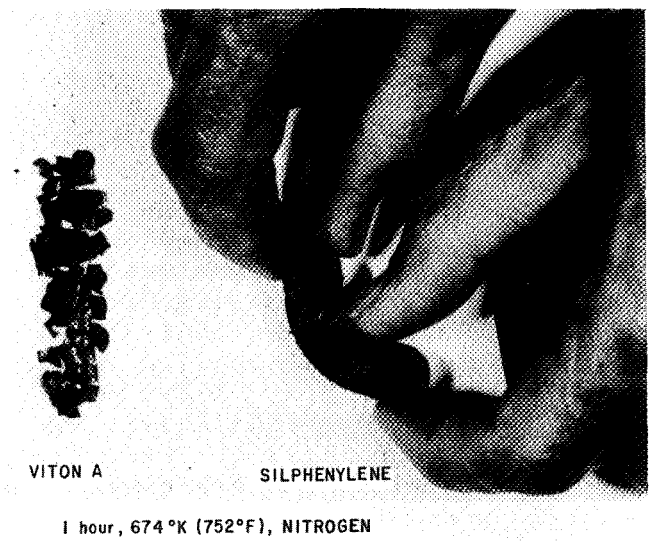


FIGURE 23. HIGH-TEMPERATURE EXPOSURE, SILPHENYLENE VERSUS VITON A

Southern Research Institute has prepared interesting variations of these polymers from silicon diols bridged by phenylene groups (Fig. 22). These materials appear to merit study as high-temperature elastomers because they respond to the same curing agents that are employed for conventional silicone rubber. In a comparison of one of the elastomers (silphenylene) with a high-temperature rubber (Viton A) under identical high-temperature exposure, the silphenylene was found to retain its elasticity while the Viton A dried and crumbled (Fig. 23).

Another idea which originated at MSFC is explained graphically in Figure 24. This appears to be a greatly improved process for the preparation of complex polymers known as polybenzoxazoles.

These polymers are not new and have been made before by a number of methods. The new feature of this process, which is the basis of another patent disclosure being submitted from the Materials Division, is the use of an aromatic diamide to form a linear polymer which is converted thermally to the highly stable polyaromatic configuration. This idea has been offered to one of our polymer research contractors who has had very good success in preparing stable polymers by this route. Although the ramifications of this explosively growing field of polymer chemistry may be discussed at much greater length, it cannot be done here. It may be noted here, however, that workers at MSFC are highly optimistic that this process will yield materials useful in many aspects of their work.

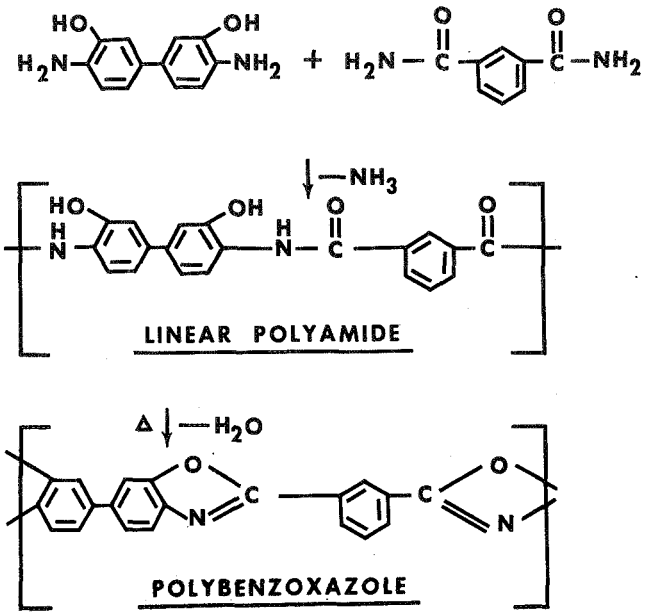


FIGURE 24. POLYBENZOXAZOLE FORMATION

2. Polymers for Low-Temperature Application. Two adhesive development programs will be discussed first. Narmco Research and Development Division of Telecomputing Corporation is continuing its original contract effort which resulted in the development of Narmco 7343, the only adhesive now available commercially that was developed specifically for cryogenic applications. The goal of this new program (NAS8-11068) is a structural adhesive that is compatible with liquid oxygen; it might be a sticky Teflon-like material which can be cured under reasonable temperature and pressure conditions. This promises to be a problem because Teflon-like materials are renowned for their lack of adhesiveness. However, the contractor has made very significant progress in the preparation of new starting intermediates which may prove capable of forming curable LOX-compatible polymers that will function as adhesives. One sample of Narmco LOX-compatible adhesive (hot melt) had a peel strength of 222 N (50 lbf) at room temperature for specimens 51 mm (2 in.) wide. This compares with 111 N (25 lbf) for a 76 mm (3 in.) specimen of HT-424.

Monsanto Research Corporation, under contract NAS8-11371, is investigating semiorganic or metal-containing polymers of potential value as adhesives. There are theoretical reasons to hope that these materials may provide usable strengths over a very broad temperature range, which may extend into the cryogenic realm.

Narmco Research and Development Division has developed an interesting new cryogenic seal material under contract NAS8-5053. Alternating plies of glass fabric and Teflon film are pressed under conditions which cause a partial flow and wetting of the fabric by the resin (Fig. 25). The resulting laminate has unique spring-like characteristics, which suggest its potential as a gasket and seal material.

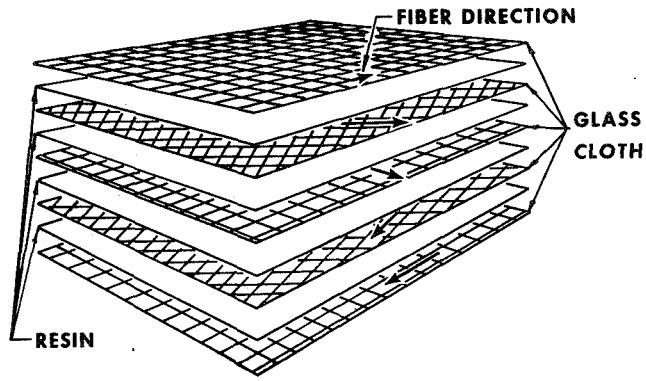


FIGURE 25. LAMINATED CRYOGENIC SEAL DEVELOPMENT

One of MSFC's oldest contract programs, and incidentally the least expensive one, has yielded some valuable information on the allowable installed lifetimes of rubber and plastic components in a semi-tropical environment. The University of Florida has a contract (NAS8-1523) to expose representative hardware containing rubber and plastic components to weather conditions in the area of Gainesville, Florida. Periodically, these valves and other items are pressure tested and cycled for evidence of seal failure due to age degradation. A parallel exposure and testing program is being conducted in the Huntsville environment by Materials Division personnel. The findings of this program have indicated that aging under the environmental conditions of concern is not as important a problem as once was thought. Consequently, the age control documentation has been relaxed, resulting in considerable saving of cost and effort.

III. ENVIRONMENTAL EFFECTS AND PROCESSES

As was indicated earlier, considerable effort is devoted to effects of processes and environments on the properties of materials. Being studied are such things as thermal and mechanical treatment of metals, corrosion protection, and compatibility of materials with working fluids. In addition to their compatibility with materials, propellants are being studied from the standpoints of mixing phenomena, reaction

kinetics, and resultant blast effects. The Materials Division of MSFC has made and continues to make a significant contribution to the knowledge of the behavior of materials, especially metals, at cryogenic temperatures. Part of its work in this area was summarized recently in a report, "Effects of Low Temperatures on Structural Metals," NASA SP-5102, prepared by the Technology Utilization Office.

At the beginning of the RIFT Program, the Materials Division initiated a study of nuclear radiation effects on nonmetallic materials under anticipated combined environments of extreme temperatures and hard vacuum. The work was concentrated on organic materials because of their greater susceptibility to degradation and because of their critical applications in a nuclear stage.

The radiation effects studies have been done primarily at General Dynamics/Fort Worth (NAS8-2450), with less extensive but equally important support from in-house studies and cooperative programs with AEC/ORNL.

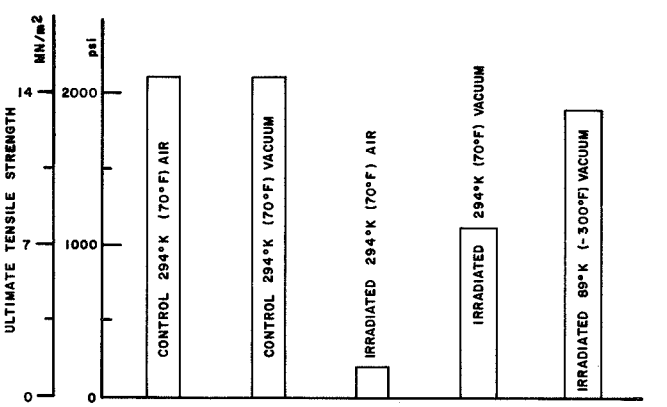
The program required the development of experimental apparatus and testing techniques that can be used under combined environmental conditions for in-situ measurements and this, alone, was a significant achievement. The devices, which are designed around standard laboratory testing methods and procedures, ensure consistency with existing data and permit direct utilization for other combined environment or hazardous testing as well as for in-flight experiments.

The evaluation of synergistic effects was necessitated because the mechanisms of material property degradation are different and competitive for the several different environments. Data on the effects of irradiating certain materials in air and in vacuum are given in Table XXI. Note the almost complete degradation of the tensile strength of neoprene and Buna N as a result of irradiation in vacuum. The Buna N became weak, tacky, and ductile as a result of the vacuum irradiation, and hard and brittle as a result of air irradiation. On the other hand, Viton A appears to be satisfactory for this environment on the basis of increased tensile strength; however, the decreased elongation would be an important consideration in the application of this material as a seal, particularly as a dynamic seal. Furthermore, Viton A is unsatisfactory for very low temperature application.

The effect of irradiating Teflon in air, vacuum, and in vacuum at a cryogenic temperature is illustrated in Figure 26. The improved stability of Teflon under the vacuum irradiation condition is well established; the combined radiation, vacuum, and cryogenic temperature environmental results, while not unexpected, were demonstrated as part of this program. The effects of irradiation of fiberglass-polyester laminate (Paraplex P-43) under several conditions are illustrated in Figure 27. As will be noticed, the effects of radiation in combination with one or more other environments cannot be determined from data for another particular combination of environments.

TABLE XXI. COMBINED ENVIRONMENTAL TESTING OF ELASTOMERS

MATERIAL	TEST	PRESSURE N/m^2(torr)	TEMP. °K(°C)	RADIATION J(ergs/gm) (C)	TENSILE STRENGTH MN/m^2 (psi)	ELONGATION PERCENT	WHERE TESTED
Neoprene (RA 24160)	Air	101 k	300	0	21.6	426	GD/FW
		(760)	(27)		(3135)		
	Vac	1.3 m	300	0	23.1	405	MSFC
		(1×10^{-5})	(27)		(3350)		
	Air/Rad	101 k	300	190	19.1	265	GD/FW
		(760)	(27)	(1.9×10^{9})	(2769)		
	Vac/Rad	667 μ	300	190	1.3	218	GD/FW
		(5×10^{-6})	(27)	(1.9×10^{9})	(191)		
Buna N (RA 30760)	Air	101 k	300	0	18.1	685	GD/FW
		(760)	(27)		(2630)		
	Vac	1.3 m	300	0	18.2	700	MSFC
		(1×10^{-5})	(27)		(2640)		
	Air/Rad	101 k	300	190	14.9	390	GD/FW
		(760)	(27)	(1.9×10^{9})	(2175)		
	Vac/Rad	667 μ	300	170	1.4	450	GD/FW
		(5×10^{-6})	(27)	(1.7×10^{9})	(203)		
Viton A (RA 26360)	Air	101 k	300	0	9.3	172	GD/FW
		(760)	(27)		(1343)		
	Vac	1.3 m	300	0	8.1	238	MSFC
		(1×10^{-5})	(27)		(1168)		
	Air/Rad	101 k	300	2000	18.1	31	GD/FW
		(760)	(27)	(2×10^{10})	(2629)		
	Vac/Rad	67 μ	316	1600	12.6	36	GD/FW
		(5×10^{-7})	(43)	(1.6×10^{10})	(1830)		



RADIATION LEVEL 100 joules/g (10^{9} erg/g) CARBON
VACUUM LEVEL 133 μN/m (10^{6} torr)

FIGURE 26. ULTIMATE TENSILE STRENGTH OF TEFLON

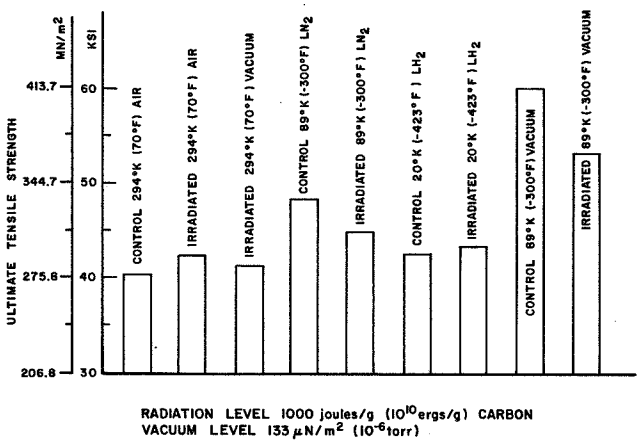


FIGURE 27. ULTIMATE TENSILE STRENGTH OF PARAPLEX P-43

Since the radiation effects testing has been done parametrically, it is believed that applicable data are now available for the design of nuclear-powered space vehicles. So that the great store of radiation effects data may be used for the design of spacecraft as well, recent work has included correlation studies between nuclear reactor radiation effects and space indigenous radiation effects.

IV. CONCLUSIONS

Some recent achievements in materials research have been discussed in this report. Some of these already have been applied in the Saturn program and others will be applied.

Although the research program has made substantial gains, all recognized problems have not been solved, and all worthy ideas for improvement have not been exploited. It is believed that the demands of advancing technology for more performance from materials will be met not by dramatic breakthroughs but by the continuous application of significant resources in a program flexible enough to allow the specialists to modify lines of investigation to take advantage of changing trends.

RESEARCH ACHIEVEMENTS REVIEW SERIES NO. 7

Materials Research at MSFC

By W. R. Lucas

The information in this report has been reviewed for security classification. Review of any information concerning Department of Defense or Atomic Energy Commission programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

This document has also been reviewed and approved for technical accuracy.

for FREDERICK B. CLINE
Director, Propulsion and Vehicle Engineering Laboratory

DISTRIBUTION

MSFC INTERNAL

DIR	1
DEP-T	1
DEP-A	1
AST-P	1
MS-H	1
CC	1
CC-P	1
LR	1
PA	2
E-DIR	6
F&D-CH	1
R-DIR	3
R-S	1
R-TS	1
R-AS	5
R-AERO-DIR (through Branch level)	30
R-AERO-T	9
R-ASTR-DIR (through Branch level)	12
R-ASTR-T	8
RP-DIR (reserve)	50

MSFC INTERNAL (Cont')

R-COMP-DIR (through Branch level)	10
R-COMP-T	5
R-ME-DIR (through Branch level)	21
R-RP-DIR (through Branch level)	8
R-P&VE-DIR (through Branch level)	29
R-P&VE-T	8
R-QUAL-DIR (through Branch level)	26
R-QUAL-T	8
R-TEST-DIR (through Branch level)	12
LVO	2
I-DIR	1
I-I/IB-MGR (through Branch level)	10
I-V-MGR (through Branch level)	10
I-E-MGR	3
I-MICH-MGR	20
I-MT-MGR	2
MS-T	25
MS-IP	2
MS-IL	8
Air Force Space Systems Division Huntsville, Alabama	1

NASA HEADQUARTERS

Dr. George E. Mueller, Code M, Washington, D. C.
Mr. Ivan Mason, Code MAT, Washington, D. C.
Dr. John M. Walker, Code RET, Washington, D. C.
Dr. Mac C. Adams, Code R, Washington, D. C.
Mr. Boyd C. Myers, Code RD, Washington, D. C.
Dr. Raymond L. Bisplinghoff, Code A, Washington, D. C.
Dr. James B. Edson, Code R-1, Washington, D. C.
Mr. Albert J. Evans, Code RA, Washington, D. C.
Dr. Walton L. Jones, Code RB, Washington, D. C.
Mr. Adelbert Tischler, Code RP, Washington, D. C.
Mr. Frank J. Sullivan, Code RE, Washington, D. C.
Mr. Harold B. Finger, Code RN, Washington, D. C.
Dr. Hermann H. Kurzweg, Code RR, Washington, D. C.
Mr. Milton B. Ames, Jr., Code RV, Washington, D. C.
Mr. E. O. Pearson, Jr., Code RV-1, Washington, D. C.
Mr. Melvin G. Rosche, Code RV-2, Washington, D. C.
Mr. Edward Z. Gray, Code MT, Washington, D. C.
Dr. Homer E. Newell, Code S, Washington, D. C.
Mr. Walter Beckwith, Code MTP, Washington, D. C.
Mr. Roland H. Chase, Code RET, Washington, D. C.
Mr. Theofolus Tsacoumis, Code RET, Washington, D. C.
Mr. Joseph L. Murphy, Code KR, Washington, D. C.
Mr. William E. Lilly, Code MP, Washington, D. C.
Gen. Samuel C. Phillips, Code MA, Washington, D. C.
Mr. Robert Freitag, Code MC, Washington, D. C.
Mr. W. Foster, Code SM, Washington, D. C.
Dr. M. Tepper, Code SF, Washington, D. C.
Dr. J. Naugle, Code SG, Washington, D. C.
Mr. E. Taylor, Code SP, Washington, D. C.
Mr. J. L. Sloop, Code RC, Washington, D. C.
Mr. Fred J. DeMeritte, Code RV-1, Washington, D. C.
Mr. William B. Taylor, Code MT, Washington, D. C.
Mr. Oliver Bumgardner, Code MTC, Washington, D. C.

CENTERS

Mr. H. Julian Allen, Director
NASA, Ames Research Center
Moffett Field, California 94035 — 2

Dr. Kurt H. Debus, Director
NASA, John F. Kennedy Space Center
Kennedy Space Center, Florida 32899 — 2

Mr. Paul F. Bikle, Director
NASA, Flight Research Center
P. O. Box 273
Edwards, California 93523 — 2

Dr. John Clark, Acting Director
NASA, Goddard Space Flight Center
Greenbelt, Maryland 20771 — 1

Dr. William H. Pickering, Director
NASA, Jet Propulsion Laboratory
4800 Oak Grove Drive
Pasadena, California 91103 — 2

Mr. Floyd L. Thompson, Director
NASA, Langley Research Center
Langley Station
Hampton, Virginia 23365 — 2

Dr. Abe Silverstein, Director
NASA, Lewis Research Center
21000 Brookpark Road
Cleveland, Ohio 44135 — 2

Mr. Warren Gillespie
Code EA 5
NASA, Manned Spacecraft Center
Houston, Texas 77001 — 15

CENTERS (Cont')

Dr. Winston E. Kock
NASA, Electronics Research Center
575 Technology Square
Cambridge, Massachusetts 02139 — 2

Mr. A. R. Lawrence
Management Analysis
NASA, Electronics Research Center
575 Technology Square
Cambridge, Massachusetts 02139 — 25

Mr. John Boyd, Technical Assistant
Office of Assistant Director for Astronautics
NASA, Ames Research Center
Moffett Field, California 94035 — 1

Mr. Chesley H. Looney, Jr., Ass't Chief
Advanced Development Division
NASA, Goddard Space Flight Center
Greenbelt, Maryland 20771 — 1

Mr. James F. Connors, Chief
Office of Research Plans and Programs
NASA, Lewis Research Center
21000 Brookpark Road
Cleveland, Ohio 44135 — 1

Mr. James E. Calkins
Office of Research and Advanced Development
NASA, Jet Propulsion Laboratory
4800 Oak Grove Drive
Pasadena, California 91103 — 1

Mr. A. R. Raffaelli
PR-2
NASA, John F. Kennedy Space Center
Kennedy Space Center, Florida 32899 — 1

CENTERS (Cont')

Mr. Robert Hinckley
NASA, Electronics Research Center
Room 323 B
575 Main Street
Cambridge, Massachusetts 02139 — 1

Dr. William G. Melbourne
Mail Stop 180-300
Jet Propulsion Laboratory
4800 Oak Grove Drive
Pasadena, California 91103 — 1

Scientific and Technical Information Facility
Attn: NASA Rep. (S-AK/RKT)
P. O. Box 33
College Park, Maryland 20740 — 25

Mr. H. M. Drake, Chief
Advanced Planning Office
NASA, Flight Research Center
Edwards Air Force Base
Edwards, California 93523 — 1

DEPARTMENT OF DEFENSE

Dr. William W. Carter
Chief Scientist
U. S. Army Missile Command
Bldg. 5250
Redstone Arsenal, Alabama — 1

Mr. John McDaniel
Technical Director
Research and Development Directorate
U. S. Army Missile Command
Bldg. 4505
Redstone Arsenal, Alabama — 12

DEPARTMENT OF DEFENSE (Cont')

Lt. M. V. Vasilik
Arnold Air Force Base
Tullahoma, Tennessee 37389 — 30

CONTRACTORS

The Boeing Company
Sahara Office Park
Huntsville, Alabama — 1

Brown Engineering Company, Inc.
300 Sparkman Drive, NW
Huntsville, Alabama — 1

Chrysler Corporation
Attention: Mr. Howard Blood
1312 Meridian, North
Huntsville, Alabama — 1

Douglas Aircraft
Holiday Office Center
Huntsville, Alabama — 1

General Electric Company
Holiday Office Center
Huntsville, Alabama — 1

Hayes International Corporation
204 Oakwood Avenue, NE
Huntsville, Alabama — 1

IBM Corporation
150 Sparkman Drive, NW
Huntsville, Alabama — 1

CONTRACTORS (Cont')

Lockheed Aircraft Corporation Holiday Office Center Huntsville, Alabama	1
North American Aviation, Inc. Holiday Office Center Huntsville, Alabama	1
Northrop Corporation Holiday Office Center Huntsville, Alabama	1
Sperry-Rand Corporation 8110 Memorial Parkway, SW Huntsville, Alabama	1
Spacecraft, Incorporated 8620 Memorial Parkway, SW Huntsville, Alabama	1
Spaco, Incorporated 3022 University Drive, NW Huntsville, Alabama	1
University of Alabama 4701 University Avenue, NW Huntsville, Alabama	1
Vitro Corporation of America Holiday Office Center Huntsville, Alabama	1
Wyle Laboratories Highway 20, West Huntsville, Alabama	1

UNIVERSITIES AND COLLEGES

Alabama A&M College Huntsville, Alabama	1
Alabama, University of Tuscaloosa, Alabama	1
Auburn University Auburn, Alabama	1
California, University of (UCLA) Los Angeles, California	1
Carnegie Institute of Technology Pittsburgh, Pennsylvania	1
Case Institute of Technology Cleveland, Ohio	1
Clemson University Clemson, South Carolina	1
Columbia University New York, New York	1
Denver, University of Denver, Colorado	1
Florida, University Gainesville, Florida	1
Georgia Tech Research Institute Atlanta, Georgia	1
Georgia, University of Athens, Georgia	1

UNIVERSITIES AND COLLEGES (Cont')

Louisiana State University Baton Rouge, Louisiana	1
Massachusetts Institute of Technology Cambridge, Massachusetts	1
Michigan, University of Ann Arbor, Michigan	1
Mississippi State University State College, Mississippi	1
Mississippi, University of University, Mississippi	1
North Carolina, University of Chapel Hill, North Carolina	1
Northeast Louisiana College Monroe, Louisiana	1
Ohio State University Columbus, Ohio	1
Ohio University Athens, Ohio	1
Oklahoma State University Stillwater, Oklahoma	1
Pittsburgh, University of Pittsburgh, Pennsylvania	1
Princeton University Princeton, New Jersey	1

UNIVERSITIES AND COLLEGES (Cont')

Purdue University Lafayette, Indiana	1
Stanford University Palo Alto, California	1
Syracuse University Syracuse, New York	1
Tennessee, University of Knoxville, Tennessee	1
Texas A&M College Station, Texas	1
Texas, University of Austin, Texas	1
Tulane University New Orleans, Louisiana	1
Vanderbilt University Nashville, Tennessee	1
Virginia Polytechnic Institute Blacksburg, Virginia	1
Washington State Pullman, Washington	1

UNITS OF MEASURE

In a prepared statement presented on August 5, 1965, to the U. S. House of Representatives Science and Astronautics Committee (chaired by George P. Miller of California), the position of the National Aeronautics and Space Administration on Units of Measure was stated by Dr. Alfred J. Eggers, Deputy Associate Administrator, Office of Advanced Research and Technology:

"In January of this year NASA directed that the international system of units should be considered the preferred system of units, and should be employed by the research centers as the primary system in all reports and publications of a technical nature, except where such use would reduce the usefulness of the report to the primary recipients. During the conversion period the use of customary units in parentheses following the SI units is permissible, but the parenthetical usage of conventional units will be discontinued as soon as it is judged that the normal users of the reports would not be particularly inconvenienced by the exclusive use of SI units."

The International System of Units (SI Units) has been adopted by the U. S. National Bureau of Standards (see NBS Technical News Bulletin, Vol. 48, No. 4, April 1964).

The International System of Units is defined in NASA SP-7012, "The International System of Units, Physical Constants, and Conversion Factors," which is available from the U. S. Government Printing Office, Washington, D. C. 20402.

SI Units are used preferentially in this series of research reports in accordance with NASA policy and following the practice of the National Bureau of Standards.